SCIENCE FOR CERAMIC PRODUCTION

FORMATION OF PERMEABLE CERAMICS WITH A GRANULAR STRUCTURE

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A mechanism of formation of a permeable ceramic structure based on a granular filler and a fine-grained sintering binder is proposed. It is observed that the finely dispersed component lowers the permeability of the structure. The impossibility of obtaining a granular permeable structure in the case of using a binder made of reaction-sintered silicon nitride is demonstrated. Permeable ceramics is produced from granulated powder, which makes it possible to avoid the fine-grained component in the volume of permeable channel-shaped pores.

Ceramics occupy a significant place among permeable porous materials. The presence of an extended system of channel-shaped pores and the possibility of making products from various materials with different porosity and structures make ceramics suitable for diverse service conditions, including aggressive media and elevated temperatures.

Numerous studies have analyzed the structure and technology of permeable ceramics [1, 2]. However, the problem of obtaining structures combining high permeability and good mechanical properties remains topical.

The purpose of our work is to study the structure formation in porous ceramic materials produced from mixtures containing a coarsely dispersed filler and a finely dispersed binder, taking two compositions as examples: coarse-grained corundum with a cordierite-bearing binder and coarse-grain corundum with a silicon nitride binder. The common technological factors include the following: the identical coarse-grained filler, the synthesis of the binder directly in the course of firing, and the final firing temperature of 1350°C; the difference consisted in the different nature of binders (cordierite and silicon nitride) having a low TCLE and ensuring usually high heat resistance.

Porous ceramics based on corundum and cordierite binder. Ceramics was produced from corundum grains with different contents of fine-grained components ensuring the synthesis of cordierite in sintering.

With a low content of the fine-grained component, large grains after firing contact each other and the emerging cordi-

erite is freely distributed mainly in the pore space between these grains. In the extreme case where all the cordierite is located in the pore space, all properties would be determined only by the properties of the corundum skeleton. Since large corundum grains do not sinter and at 1350°C do not even perceptibly fuse to each other, the strength of such ceramics would be minimal and the TCLE would be equal to the TCLE of corundum, i.e., 8.5×10^{-6} K^{-1}. In reality part of the emerging cordierite is located on the sites of contact of large grains ensuring some strength, a decrease in the TCLE, and an increase in thermal resistance.

As the cordierite content grows, it gradually fills all pore space between the corundum grains and then starts pushing apart these grains, thus forming an apparently continuous cordierite matrix with incorporated corundum grains. In the extreme case where all the corundum grains are separated, all the main properties of such ceramics would be determined by the properties of cordierite.

One should note the structural specifics of ceramics considered, which is related to the coexistence of two phases with significantly different values of thermal expansion and thermal compression after cooling of ceramics [3]. Cordierite in firing is synthesized in the final stages of heat treatment and is localized on corundum grains expanded under heating. After cooling, the corundum grains shrink more than cordierite grains whose thermal expansion (about 2×10^{-6} K^{-1}) is significantly lower than that of corundum, i.e., the cordierite phase in cooling inevitably becomes separated from the corundum grains and forms microclearances whose size further increases due to the shrinkage of cordierite in sintering. The

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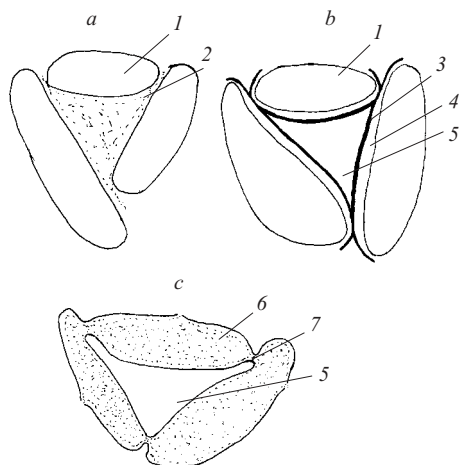
Fig. 1. Schematic structure of permeable ceramics: *1*) filler grain; *2*) fine-grained fraction; *3*) sintered binder; *4*) microclearance; *5*) channel-shaped pore; *6*) granule; *7*) bridge.

Fig. 2. Equal strength (dashed) and equal gas permeability (solid) lines. Digits at the straight lines indicate compression strength (MPa) and gas permeability (μm^2).

formation of microclearances is observed starting with 10 vol.% content of the fine component.

Thus, the final structure of corundum-cordierite porous ceramics depends on the initial structure of the unfired preform determined by the size of packing of corundum grains, the concentration of the fine-grained component, the molding pressure, and modifications occurring after the synthesis of cordierite and cooling of ceramics.

In this case the coarse-grained filler at the molding stage acts as a regulator of the size and shape of permeable pores, whereas the emerging cordierite creates a skeleton matrix ensuring all the main characteristics of such ceramics, primarily its strength, TCLE, and thermal resistance (Fig. 1). The emerging structure combining coarse filler grains, the cordierite binder, and a complex system of pores and microclearances determines the total porosity, pore size and distribution, and eventually the final gas permeability. The latter to a certain extent can be controlled by varying the initial parameters of ceramic mixtures and heat treatment conditions.

However, such technology does not ensure very high gas permeability. Gas permeability can be increased by increasing the content of the filler grains at the expense of decreasing the content of the fine-grained component or by decreasing molding pressure, but this inevitably decreases strength and leads to changes in other technical properties (Fig. 2).

Porous ceramics based on corundum with nitride binder. This ceramics was produced similarly to the cordierite-bearing ceramics, but the fine fraction was represented by milled silicon taken in different quantities, and firing was performed in a nitrogen medium to synthesize silicon nitride from silicon to be used as a binder for corundum grains.

Before firing the structure of preforms is similar to that of cordierite-bearing samples (Fig. 1*a*). i.e., silicon up to a certain content is localized inside the pore space between the corundum grains and then starts pushing them apart, forming a silicon matrix, in which the filler grains exist.
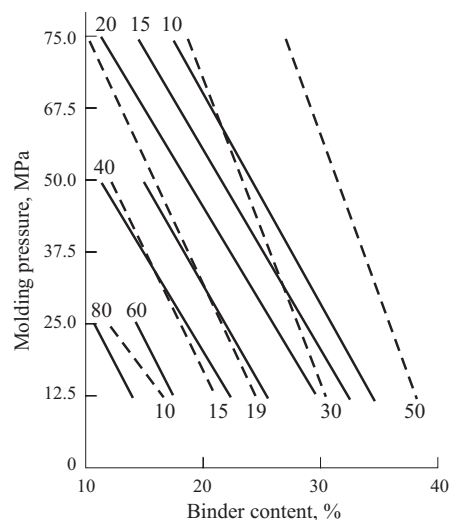
Silicon nitride is formed by reaction sintering in a nitrogen medium. Since the reaction between silicon and nitrogen has a positive volume effect, the formation of silicon nitride is accompanied by increasing the sample volume by 23%, i.e., the fine-grained component does not shrink, as in the cordierite variant, but grows in volume. At the same time, the structure of the sample virtually does not change.

Consequently, silicon nitride is formed at the final firing temperature and is localized on corundum grains expanded under heating. After cooling, as a result of the difference in the TCLEs of corundum and silicon nitride ($8.5 \times 10^{-6} K^{-1}$ and $3 \times 10^{-6} K^{-1}$, respectively) the nitride layers get separated from the corundum grains as well, but the size of clearances is smaller, since silicon nitride grows in volume under firing.

As for the silicon nitride matrix, when the silicon content is substantial, the pore size decreases while silicon transforms into silicon nitride. The strength of ceramics in this case grows perceptibly and its gas permeability, accordingly, decreases (Fig. 3). With increasing content of silicon and silicon nitride, the TCLE gradually decreases reaching approximately $3 \times 10^{-6} K^{-1}$, which is typical of silicon nitride.

The gas permeability for two types of binders with contents equal to 10 and 23% for the cordierite-bearing binder amounts to 80 and 13 μm^2, respectively, (1 μm^2 = 10 nPm) and for the nitride-bearing binder 20 and 0 μm^2, i.e., with a silicon nitride content equal to 23% gas permeability is absent. In any case gas permeability in cordierite-bearing ceramics is generally low and in nitride-bearing ceramics it tends to zero.

Thus, it is impossible to obtain porous ceramics by the standard method even using large filler grains, since the introduction of fine fractions required for binding large filler grains leads to an abrupt decrease in the gas permeability of ceramics.

In this context the problem arises of forming a permeable ceramic structure while preserving the advantages of the method of choosing a granular composition (the presence of an extended system of variable-section communicating channel pores) and eliminating its negative aspects (the presence of the fine-grained component inside the channel pore volume). The solution of this problem becomes even more topical considering that it is impossible to apply the method of choosing a granular composition to producing permeable structure from a number of materials with valuable properties (mechanical strength, temperature resistance, chemical resistance to different media) such as, for instance, silicon nitride.

Method of using granulated powders. Porosity and gas permeability can be increased by introducing burn-out additives; however, this significantly decreases strength, which is not acceptable.

As a result of experiments with mixtures based on the granular filler and the fine-grained component, it has been found that the latter is needed only at the sites of contact between large grains for their binding. The majority of fine fractions (in our case cordierite and silicon nitride) contained in the pore space between large corundum grains have no positive effect. On the contrary, they lower the porosity and gas permeability of ceramic structures.

However, it is impossible to distribute the coarse and fine fractions in such a way that the latter are located only at the contact sites of large grains.

In order to preserve the permeable channel pore structure both at the stage of molding and after firing and to ensure sufficiently high strength, we studied the production of permeable ceramics using granulated powders (USSR Inventor's Certif. No. 990724). For this purpose fine-grained powders were subjected to granulation. This method makes it possible to obtain isometric and nonisometric granules of different sizes from virtually any material.

Preforms molded of such granules are subjected to heat treatment at a preset temperature. Since the granules consist of fine fractions, they intensely sinter to each other in firing, whereas large pores created by granule packing already at the stage of molding are preserved and do not become filled with fine fractions. (Fig. 1c).

Thus, the use of granules makes it possible to preserve high permeability due to channel-shaped pores, whereas the accretion of granules in firing ensures substantial strength.

Granule-based ceramic materials have been produced from porcelain mixture, cordierite, aluminum oxide, silicon nitride, and from mixtures of different compositions in the silicon dioxide – aluminum oxide system. The resulting porous ceramics have increased permeability. By varying the size and shape of granules it is possible to obtain permeable ceramics with a wide (from 25 to 2500 μm^2) gas permeability range, which is impossible using the standard method combining large filler grains with fine fractions.
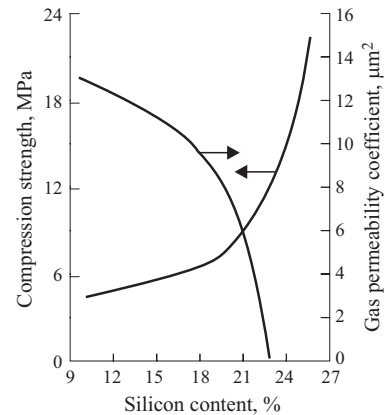

Fig. 3. Variation in compression strength and gas permeability of nitride samples depending on silicon content.

Granule-based ceramics also have increased fluid permeability, Thus, corundum-cordierite ceramics containing 10% cordierite phase has water permeability $4.7 \times 10^{-2}\ \mu m^2$, whereas the water permeability of ceramics based on granules of size $200 – 500\ \mu m$ is equal to $20\ \mu m^2$, i.e., more than 400 times higher. When the granule size was increased, the water permeability of the ceramics grew to $300\ \mu m^2$.

Despite such high permeability, porous ceramic based on granules has good capacity for entrapping solid particles suspended in the liquid, due to the high tortuosity of the channel pores and the high labyrinth factor, i.e., they can be used as efficient filters to purify liquids and metal melts.

The filter efficiency depends on the granule size and the thickness of the filtering element. The smaller the granule size and the thicker the element, the finer is the purification, although the rate of filtration in this case inevitably declines. The effect of these factors is shown in Table 1.

The strength of granule-based ceramics depends insignificantly on the material of granules and is perceptibly higher than the strength of traditional granular-structure ceramics. Thus, the compression strength of ceramics with porosity 40%

TABLE 1

Sample height, cm	Quantity of particles passing through filter,[*] %, under their maximum size, μm						
	100	60	50	40	28	14	10
Average granule size 1.50 mm							
1.0	0	76.5	90	100	100	100	100
4.0	0	0	0	10	37	56	100
Average granule size 0.75 mm							
1.5	0	0	0	13	40	70	100
4.0	0	0	0	2	14	33	70
Average granule size 0.38 mm							
1.0	0	0	0	0	0	23	60
4.0	0	0	0	0	0	0	1

[*] With sample height of 1.0 and 2.5 mm and average granule size 0.10 mm all particles were retained.

made of granules of size 0.38 mm is equal to 17 MPa, whereas the strength of ceramics with porosity 32.5% made of corundum grains of size 0.40 mm is 12 MPa.

Thus, a method for producing permeable ceramic from granulated silicon nitride powder has been developed. The fine-grained component has a double role: first, it is used to mold granules whose packing provides for a system of channel-shaped pores; second, it provides for a continuous compacted powder structure in the whole volume of the preform already at the molding stage.

The use of granulated powders makes it possible to produce ceramics with a widely variable permeability and a high filtering capacity, which makes it suitable for fast filtration of liquids and metal melts.

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